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IS 1448-55 (2004): Methods of test for petroleum and its products, Part 55: Saponification value, saponifiable and unsaponifiable matter [PCD 1: Methods of Measurement and Test for Petroleum, Petroleum Products and Lubricants]

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IS : 1448 [P : 55] - 1963
Adopted : 21 *December* 1963
(Reaffirmed 2002)

Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

[P : 55]

SAPONIFICATION VALUE, SAPONIFIABLE AND UNSAPONIFIABLE MATTER

(Third Reprint FEBRUARY 1985)

UDC 621·892·2 : 543·851·5

Adapted, with permission, from the Institute of Petroleum Standard No. IP 136/63 and from ASTM D 939-54

[The methods given in P : 55 will supersede those in L : 10 of IS : 310 (Part I) - 1951*]

1. SCOPE

1.1 These methods are intended for the determination of saponification value and saponifiable and unsaponifiable matter present in straight mineral oils, compounded mineral oils and waxes.

2. TERMINOLOGY

2.1 Saponification Value — The number of milligrams of potassium hydroxide required to saponify one gram of the sample under conditions of this test.

2.2 Unsaponifiable Matter — The fraction of substances in fats or oils which are not saponified by caustic alkali but are soluble in ordinary fat-solvents.

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*Methods of sampling and test for lubricants, Part I.

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3. METHODS

3.0 Three methods, namely, volumetric, gravimetric, and potentiometric methods have been prescribed in this method.

3.1 Method A (Volumetric) — This method may be used to determine small amounts of saponifiable matter in mineral oil (*see* Note 1). When the saponification value of the saponifiable constituents of a blend is known, this method may be used to determine the amount of saponifiable matter in the blend. If the saponification value of the saponifiable constituents of the blend is not known, the method can be used, but the result can be expressed only as a saponification value.

3.1.1 This method is not applicable in the presence of compounds of sulphur, phosphorus, chlorine, or other elements which react with acid or alkali (*see* Note 2).

NOTE 1 — Experience has shown that for transformer oils, Method A modified by the use of 0·1 N alcoholic potassium hydroxide solution and 0·1 N hydrochloric acid, is more suitable.

NOTE 2 — The odour of hydrogen sulphide detected towards the end of the titration is an indication of the presence of reactive sulphur compounds in the sample and that the saponification value obtained will be greater than that due to the amount of fatty matter actually present. Unfortunately, reactive chlorine and phosphorus compounds give no such simple indication during the test.

3.2 Method B (Gravimetric) — This method may be used to determine the unsaponifiable and saponifiable matter in blends of mineral and fatty oils, particularly when the nature of the saponifiable oil is not known. It is also suitable for essentially fatty materials. This method shall, however, be used when compounds of sulphur, phosphorus, chlorine or other elements which react with acid or alkali are present.

3.2.1 This method is not applicable in the following cases:

a) If the sample contains products saponifiable with difficulty, such as certain waxes, resins, or esters of higher fatty acids which form sparingly soluble potassium salts;

b) If the sample contains unsaponifiable constituents of high melting point and low solubility in ether; and

c) If the sample contains highly polymerized fatty oils which form emulsions that can be separated only with difficulty. In this case, the procedure may become very cumbersome, if not impossible.

3.2.2 The fatty acids and unsaponifiable matter isolated in this method may be examined for identification if this is desired.

3.3 Method C (Potentiometric) — This method is intended particularly for the determination of saponification value of new or used oils, electrical oils, and greases whether compounded or not. It is useful for the identification of unmixed animal or vegetable oils and for the determination of the amount of fatty material in compounded products, provided the sample does not contain appreciable amounts of certain non-fatty compound, such as those of sulphur, phosphorus, the halogens, nitrogen, and metals other than potassium or sodium, which consume alkali or acid under the conditions of the test.

4. OUTLINE OF THE METHODS

4.1 In *Method A* a known weight of the sample is heated with a known amount of alkali solution so that the fat is saponified. Excess alkali is titrated with standard acid and the saponification value calculated.

4.2 In *Method B* the weighed sample is also saponified with alkali solution, but the unsaponifiable matter is separated and weighed. The fatty acids are liberated, separated, and weighed.

4.3 In *Method C* the weighed sample is dissolved in a mixture of benzene and *iso*propyl alcohol and saponified by refluxing for two hours with an excess of potassium hydroxide. The excess of potassium hydroxide is then titrated potentiometrically with alcoholic hydrochloric acid solution, using a glass indicating electrode and a calomel reference electrode. The meter readings are plotted against the respective volumes of titrating solution and the end points are taken at the inflections in the resulting curve. When no definite inflections are obtained, end points are taken at meter readings corresponding to those found for standard non-aqueous acidic and basic buffer solutions.

5. METHOD A (VOLUMETRIC)

5.1 Apparatus

5.1.1 *Reaction Flask* — conical flask of 300-ml capacity, of alkali-resistant glass and chemically clean. Flasks which have become etched by long use should not be used.

5.1.2 *Reflux Condenser* — a water condenser.

5.1.3 *Hot-Plate*

5.2 Reagents and Materials

5.2.1 *Purified Rectified Spirit* — Dissolve 1·5 g of silver nitrate in about 3 ml of water, add one litre of rectified spirit (*see* IS : 323-1959*) in a glass-stoppered bottle, and mix thoroughly. Mix 3 g of potassium hydroxide in 10 to 15 ml of warm rectified spirit. Cool, and add slowly to the alcoholic silver nitrate solution with slight stirring. Allow the precipitated silver oxide to settle, siphon off the clear supernatant solution, and distil on a steam-bath.

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*Specification for rectified spirit (*revised*).

5.2.2 *Alcoholic Potassium Hydroxide Solution* — approximately 0·5 N (*see* Note 3). Dissolve 30 g of potassium hydroxide in one litre of purified rectified spirit and allow the solution to settle in a dark place. Decant or filter the clear solution through glass wool and allow the solution to stand for 20 hours before use.

5.2.3 *Standard Hydrochloric Acid* — 0·5 N (*see* Note 3).

Note 3 — Where saponification values below 1 (for example, of transformer oils) are expected, better precision may be obtained by substituting 0·1 N potassium hydroxide and hydrochloric acid for these reagents.

5.2.4 *Phenolphthalein Indicator* — Dissolve 0·1 g of phenolphthalein in 100 ml of 60 percent purified rectified spirit.

5.2.5 *Methyl Ethyl Ketone* — technical grade. It should be stored in a dark place.

5.2.6 *Petroleum Hydrocarbon Solvent* (60/80) — boiling between 60°C and 80°C.

or

5.2.7 *n-Heptane*

5.3 Procedure

5.3.1 Use such a quantity of the sample that not more than half of the potassium hydroxide in the reagent added reacts during the test. The following quantities are suggested:

For fats and fixed oils	2 g
For blends containing 70 percent fats	3 g
For blends containing 30 percent fats	5 g
For blends containing 10 percent fats	10 g
For mineral oils	20 g

5.3.2 Weigh the oil sample to the nearest 0·1 percent into a reaction flask. Add 25 ± 1 ml of methyl ethyl ketone followed by 25·00 ± 0·03 ml of the alcoholic potassium hydroxide solution measured accurately from a burette. Connect the condenser to the flask and heat for 30 minutes after refluxing begins (*see* Note 4). Immediately disconnect the condenser, cautiously add 50 ml of the petroleum hydrocarbon solvent or *n*-heptane (*see* Note 5) and at once titrate the solution with standard hydrochloric acid, using 1 ml of phenolphthalein indicator. When testing waxes it may be necessary to re-heat during titration in order to prevent solidification of the sample.

Note 4 — For most oils refluxing for 10 minutes is sufficient to complete saponification, and if it is known that the material is free from oils requiring longer saponification then the time may be reduced to this value, the reflux time for blank being equally reduced.

Note 5 — In the case of transformer and similar types of mineral oil, the use of petroleum hydrocarbon solvent or *n*-heptane is unnecessary.

5.3.3 Make a blank determination in duplicate at the same time following exactly the same procedure but omitting the sample.

5.4 Calculation

5.4.1 Calculate the saponification value of the sample from the following equation:

$$S = \frac{56 \cdot 1\ (V_1 - V)\ N}{W}$$

where

S = saponification value of the sample,

V_1 = mean volume in ml of standard hydrochloric acid used in the blank,

V = volume in ml of standard hydrochloric acid used in titration,

N = normality of the standard hydrochloric acid, and

W = weight in g of sample used.

5.4.2 Calculate the percentage of fatty oil in the sample from the saponification value by using the expression:

$$\text{Fatty oil, percent by weight} = \frac{100\ S}{F}$$

where

F = saponification value of the fatty oil present in the sample.

5.4.3 The saponification value for several fatty oils are given below:

Arachis oil	190	Tallow	195
Castor oil	180	Sperm oil	130
Olive oil	190	Shark-liver oil	165
Rape oil	175	Whale oil	193
Lard oil	195	Coconut oil	260

5.5 Reporting — Report the result to the nearest 0·5 as the saponification value (**P : 55**) Method A. For transformer oils, report to the nearest 0·1.

5.6 Precision

5.6.1 Results of duplicate tests shall not differ by more than the following amounts:

	Repeatability	*Reproducibility*
For fats and fixed oils	2·0	4·0
For blends containing over 30 percent fats	1·0	2·0
For blends containing less than 30 percent fats	0·5	1·0

For highly coloured oils the variations may be double these figures. When using 0·1 N reagents the precision limits are:

Repeatability	0·2
Reproducibility	0·4

5.6.2 As the percentage of saponifiable matter is obtained by calculation from the saponification value, this will be subject to proportionate variation.

6. METHOD B (GRAVIMETRIC)

6.1 Apparatus — same as given under **5.1**.

6.2 Reagents

6.2.1 *Potassium Hydroxide* — solid.

6.2.2 *Purified Rectified Spirit* — *See* **5.2.1**.

6.2.3 *Diethyl Ether* — free from peroxides.

6.2.4 *Hydrochloric Acid* — concentrated (conforming to IS : 265-1962*)

6.2.5 *Dilute Hydrochloric Acid* — approximately 3 N.

6.2.6 *Methyl Orange Indicator* — Dissolve 0·01 g of methyl orange in water and dilute to 100 ml.

6.2.7 *Phenolphthalein Indicator* — same as in **5.2.4**.

6.2.8 *Anhydrous Sodium Sulphate* — freshly ignited at 650°C and subsequently cooled in an empty vacuum desiccator before use.

6.2.9 *Sodium Sulphate Solution* — Dissolve 10 g of the hydrated salt in water and make up the volume to 100 ml.

6.2.10 *Potassium Hydroxide Solution* — approximately 0·5 N.

6.2.11 *Standard Sodium Hydroxide Solution* — 0·1 N.

6.2.12 *Acetone* — dry.

6.3 Safety Precautions

6.3.1 It is necessary to ensure that the handling of diethyl ether is carried out away from flames or other sources of heat as this solvent is extremely inflammable Electric ovens with internal make-and-break contacts shall not be used for removing traces of ether.

6.3.2 During ether extractions, take care to release the pressure at frequent intervals.

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*Specification for hydrochloric acid (*revised*).

6.4 Procedure

6.4.1 Use a quantity of sample such that not more than half of the potassium hydroxide added reacts during the test (*see* Note 6). The following quantities are suggested:

For oils containing more than 70 percent fatty matter	2 g	approximately
For oils containing 30 to 70 percent fatty matter	5 g	„
For oils containing less than 30 percent fatty matter	10 g	„

NOTE 6 — If larger amounts of unsaponifiable or saponifiable matter are required for further examination, larger samples may be taken provided the quantities of the reagents are suitably adjusted.

6.4.2 Weigh the oil sample to the nearest 0·1 percent into the reaction flask. Add 50 ml of purified rectified spirit and about 3 g of potassium hydroxide. Connect the flask to the reflux condenser and boil the contents gently for 3 hours; one hour is sufficient for pure fatty oils. Before disconnecting the flask, wash down the condenser with 10 ml of purified rectified spirit. Cool the contents of the flask and transfer these to a chemically clean 500-ml separating funnel. Rinse the flask with 150 ml of water and transfer the rinsings to the separating funnel. Rinse the flask with successive portions of ether to a total of 50 ml and transfer each portion to the separating funnel.

6.4.3 Shake the mixture (**Caution** — *see* **6.3.2**) and allow the funnel to stand until the two layers of liquid separate and clarify. Draw off the lower (aqueous-alcoholic) layer into the reaction flask used for saponification.

6.4.4 Pour the ethereal layer from the top of the funnel into a second chemically clean 500-ml separating funnel containing 20 ml of water. However, if the ether layer contains any solid suspended matter, it shall be filtered into the funnel using a small, dry fat-free filter; wash the filter subsequently with small amounts of ether and allow the washings to run into the main ether layer. Transfer the aqueous-alcoholic layer back to the first funnel and extract twice more with 50-ml portions of ether. After each extraction run the aqueous-alcoholic solution back into the reaction flask. Add each ether layer in turn to the second funnel, filtering if necessary. Shake the contents of the second funnel gently, allow the layers to separate, then run off the water into the aqueous-alcoholic solution in the reaction flask.

6.4.5 *Unsaponifiable Matter* — Add 5 drops of the hydrochloric acid to the contents of the second separating funnel and shake it vigorously. Wash the ethereal solution with 20 ml of water and reject the washings.

6.4.6 Wash the ethereal solution with a further 20 ml of water and transfer these washings to the first separating funnel. Make three successive washings with 20 ml of potassium hydroxide solution, then wash with 20-ml portions of water until the washings are no longer alkaline to phenolphthalein indicator. Add all these washings to the first funnel.

6.4.7 Transfer the ethereal solution from the second funnel to a chemically clean 600-ml beaker, rinse the funnel with a little ether and add to the beaker. Add 20 ml ether to the first funnel, shake gently and allow the phases to separate. Transfer the aqueous layer to the second funnel and wash the ether layer in the first funnel with successive 5 ml portions of water until the washings are no longer alkaline to phenolphthalein indicator. Add all the washings to the second funnel and transfer the ether layer to the main ether extract in the 600-ml beaker.

6.4.8 Dry the ethereal solution in the 600-ml beaker over ignited sodium sulphate until it is clear and bright, covering the beaker with a clock-glass. Transfer the solution through a dry fat-free filter-paper into a tared wide-necked flask washing the sodium sulphate with a little dry ether. Distil off the ether on a steam-bath (*see* Note 7) (**Caution** — *see* **6.3.1**). Heat the flask in an oven at a temperature of 80°C until it is substantially constant in weight and record the weight of the contents of the flask. Add 10 ml of purified rectified spirit, neutralized to phenolphthalein indicator, and swirl to dissolve the contents. Add a few drops of phenolphthalein indicator and titrate with standard sodium hydroxide solution to the usual pink end point. The titration should not exceed 0·1 ml. If it does, reject the test and repeat from the beginning.

Note 7 — If it is known or suspected that very volatile hydrocarbons are present, it is recommended that they should be removed from the original material with the aid of some form of diluent trap, the non-volatile residue being subjected to the procedure described above.

6.4.9 *Saponifiable Matter* — Combine the aqueous-alcoholic solution in the reaction flask with the bulked washings from the second funnel in a 600-ml beaker and evaporate down to a convenient volume (*see* Note 8). Cool, transfer to a clean 500-ml separating funnel and acidify with an excess of dilute hydrochloric acid.

Note 8 — It is not necessary to remove all alcohol from the aqueous liquor; provided that the concentration of alcohol does not exceed 30 percent by volume, no inconvenience should be experienced.

6.4.10 Add 50 ml of ether to the contents of the funnel, shake and allow the phases to separate. Draw off the acid-layer into a beaker and pour the ether layer from the top of the funnel into a second funnel containing 20 ml of sodium sulphate solution. Repeat the ethereal extraction of the acid liquor twice more using in each case 50 ml of ether, combining the ether extracts in the second funnel. Shake the contents of the second funnel, allow them to separate and run off the sodium sulphate layer. Add a further 20 ml of the sodium sulphate solution and repeat the procedure until the washings no longer give an acid reaction with methyl orange indicator.

6.4.11 Dry the ethereal solution over anhydrous sodium sulphate until it is clear and bright, covering the beaker with a clock-glass. Filter it into a tared wide-necked flask, washing the sodium sulphate with a little dry ether. Remove the ether by distillation on a steam-bath (**Caution** — *see* **6.3.1**). When all the ether is apparently removed, add 5 ml of acetone to the contents of the flask and warm it on the water-bath for approximately one minute. Remove the flask from the bath and then, while rotating the flask at an angle of about 45°, direct a gentle current of air into the mouth of the flask for approximately one minute to remove the bulk of the acetone.

6.4.12 Place the flask in an explosion-proof oven at 80°C for 10 minutes. Remove the flask from the oven, blow it with air as before for about 15 seconds (*see* Note 9) and allow the flask to cool in a desiccator for 10 minutes before weighing. Repeat this procedure until the difference between two consecutive weighings does not exceed 5 mg. Remove the last traces of ether by heating the flask in an oven at 100°C for not more than 30 minutes and then by blowing with a gentle current of air. Cool and weigh the flask. Record the weight of the contents of the flask.

NOTE 9 — If it is known that the fatty acids are very susceptible to oxidation, for example, linseed fatty acids, drying in a current of inert gas is advisable.

6.4.13 A diagrammatic outline of this procedure is shown in Fig. 1.

6.5 Calculation and Reporting

6.5.1 Calculate the results as percentages of the sample and report them to the nearest 0·1 as the unsaponifiable matter and saponifiable matter (**P : 55**) Method B.

6.6 Precision

6.6.1 *Unsaponifiable Matter* — No precision limits can be established, since the volatility of the unsaponifiable matter may vary widely with different products.

6.6.2 *Saponifiable Matter* — Results of duplicate tests shall not differ by more than the following amounts:

Fatty Acid, Percent by Weight	*Repeatability*	*Reproducibility*
Above 5	10 percent	10 percent
Below 5	Not established	Not established

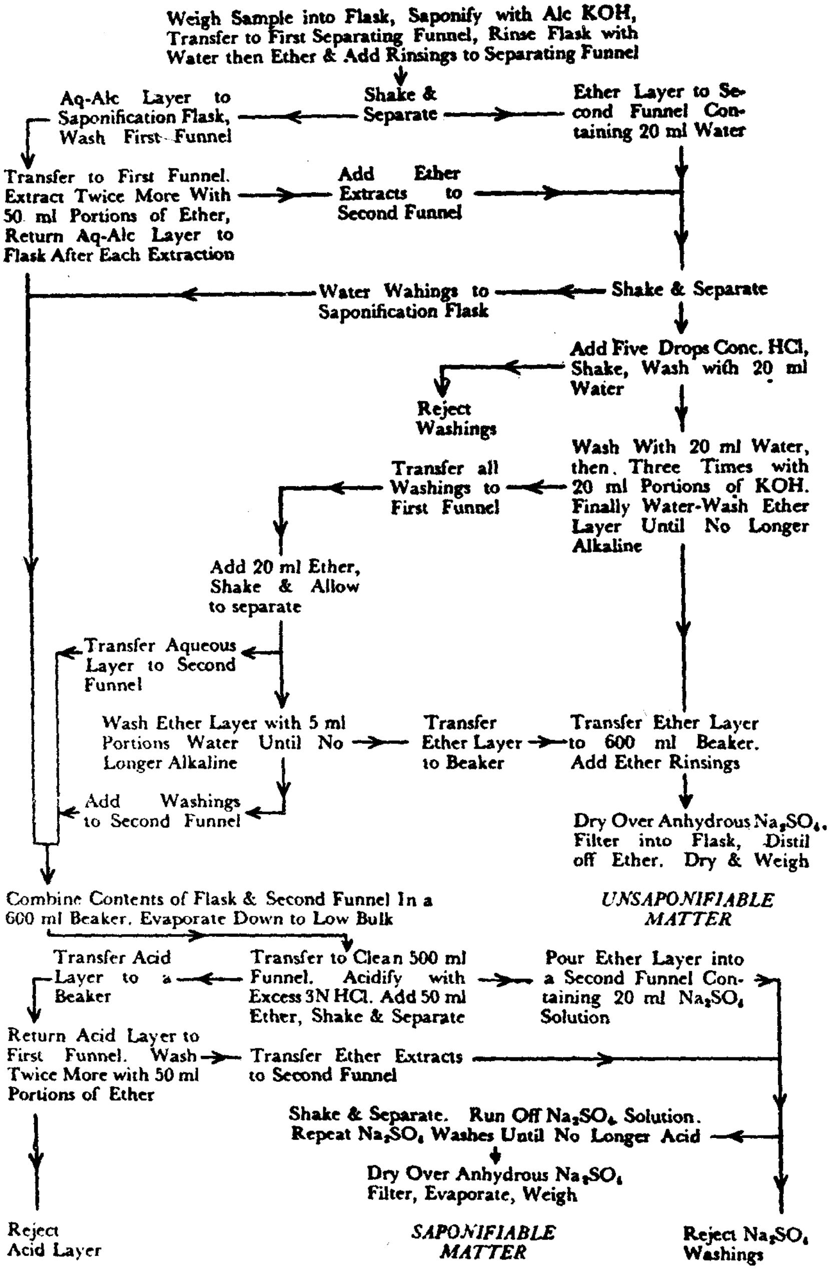
Weigh Sample into Flask, Saponify with Alc KOH, Transfer to First Separating Funnel, Rinse Flask with Water then Ether & Add Rinsings to Separating Funnel
Shake & Separate
Aq-Alc Layer to Saponification Flask, Wash First Funnel
Ether Layer to Second Funnel Containing 20 ml Water
Transfer to First Funnel. Extract Twice More With 50 ml Portions of Ether, Return Aq-Alc Layer to Flask After Each Extraction
Add Ether Extracts to Second Funnel
Water Wahings to Saponification Flask
Shake & Separate
Add Five Drops Conc. HCl, Shake, Wash with 20 ml Water
Reject Washings
Wash With 20 ml Water, then, Three Times with 20 ml Portions of KOH. Finally Water-Wash Ether Layer Until No Longer Alkaline
Transfer all Washings to First Funnel
Add 20 ml Ether, Shake & Allow to separate
Transfer Aqueous Layer to Second Funnel
Wash Ether Layer with 5 ml Portions Water Until No Longer Alkaline
Transfer Ether Layer to Beaker
Transfer Ether Layer to 600 ml Beaker. Add Ether Rinsings
Add Washings to Second Funnel
Dry Over Anhydrous Na_2SO_4. Filter into Flask, Distil off Ether. Dry & Weigh
Combine Contents of Flask & Second Funnel In a 600 ml Beaker. Evaporate Down to Low Bulk
UNSAPONIFIABLE MATTER
Transfer Acid Layer to a Beaker
Transfer to Clean 500 ml Funnel. Acidify with Excess 3N HCl. Add 50 ml Ether, Shake & Separate
Pour Ether Layer into a Second Funnel Containing 20 ml Na_2SO_4 Solution
Return Acid Layer to First Funnel. Wash Twice More with 50 ml Portions of Ether
Transfer Ether Extracts to Second Funnel
Shake & Separate. Run Off Na_2SO_4 Solution. Repeat Na_2SO_4 Washes Until No Longer Acid
Dry Over Anhydrous Na_2SO_4 Filter, Evaporate, Weigh
Reject Acid Layer
SAPONIFIABLE MATTER
Reject Na_2SO_4 Washings

FIG. 1 DIAGRAMMATIC OUTLINE OF METHOD B

7. METHOD C (POTENTIOMETRIC)*

7.1 Apparatus

7.1.1 *Cell Assembly* — Consisting of glass electrode, calomel electrode, stirrer, burette, beaker and stand. The cell assembly is shown in Fig. 2 and its different parts are described in **7.1.1.1** to **7.1.1.6.**

7.1.1.1 *Glass electrode* — a pencil type glass electrode (*see C* in Fig 2), 125 to 180 mm in length and 8 to 14 mm in diameter. The body of the electrode shall be made of a chemically-resistant glass tube with a wall thickness of 1 to 3 mm. The end dipping into the solution shall be closed with a hemisphere of a chemically-resistant glass† sealed on to the electrode tube and the radius of this hemisphere shall be about 7 mm. The thickness of the glass in the hemisphere shall be great enough so that the resistance of the hemisphere is 100 to 1 000 megohms at 25°C. The electrode shall contain a reproducible, permanently sealed liquid cell for making electrical connection with the inner surface of the hemisphere. The entire electrical connection from the sealed contact cell to the meter terminal shall be surrounded by an electrical shield that will prevent electrostatic interference when the shield is grounded. The shield shall be insulated from the electrical connection by insulating materials of the highest quality, such as rubber and glass, so that the resistance between the shield and the entire length of the electrical connection is greater than 50 000 megohms.

7.1.1.2 *Calomel electrode* — a pencil type calomel electrode (*see B* in Fig. 2), 125 to 180 mm in length and 8 to 14 mm in diameter. This electrode shall be made of glass and shall be provided with an external, removable glass sleeve on the sealed end which is dipped into the titration solution. The glass sleeve shall be 8 to 25 mm in length, slightly tapered, and shall be ground to fit the electrode so that the sealed end of the electrode protrudes 2 to 20 mm beyond the sleeve. The ground surface shall be continuous and free from smooth spots. At a point midway between the extremities of the ground surface, the electrode tube shall be pierced by one or more holes each one millimeter in diameter. The electrode shall contain the necessary mercury, calomel, and electrical connection to the mercury, all arranged in a permanent manner. The electrode shall be filled almost to capacity with saturated potassium chloride electrolyte and shall be equipped with a stoppered port through which the electrolyte may be replenished. When suspended in the air and with the sleeve in place, the electrode shall not leak electrolyte at a rate greater than one drop in 10 minutes.

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*Adapted from ASTM Designation: D 939-54.

†Corning 015 glass is suitable.

7.1.1.3 *Stirrer* — a variable speed mechanical stirrer of any suitable type, equipped with a glass propeller type stirring paddle (*see D* in Fig. 2). A propeller with blades 6 mm in radius and set at a pitch of 30 to 45 degrees is satisfactory. If electrical stirring apparatus is used, it shall be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in meter reading during the course of the titration.

7.1.1.4 *Burette* — a 50-ml burette (*see E* in Fig. 2) graduated in 0·1 ml divisions. With an elongated tip which extends to 100 to 130 mm beyond the glass stop-cock shall be used.

7.1.1.5 *Titration beaker* — a 300-ml, tall form, lipless beaker (*see A* in Fig. 2) made of chemically-resistant glass. The beaker shall be 116 to 120 mm in height and 62 ± 3 mm inside diameter below the flared portion with sides tapering in at an angle of approximately one degree from the vertical.

7.1.1.6 *Titration stand* — a suitable stand to support the electrodes, stirrer, and burette in the position shown in Fig. 2. An arrangement that allows the removal of the beaker without disturbing the electrodes, burette, and stirrer is desirable.

7.1.2 *Meter* — a voltmeter or potentiometer that will operate with an accuracy of ± 0·005 V and a sensitivity of ± 0·002 V over a range of at least ± 0·5 V, when the meter is used with the electrodes specified in **7.1.1.1** and **7.1.1.2** and when the resistance between the electrodes falls within the range of 0·2 to 20 megohms. The meter shall be protected from stray electrostatic fields so that no permanent change in the meter readings over the entire operating range is produced by touching, with a grounded* lead, any part of the exposed surface of the glass electrode, the glass electrode lead, the titration stand, or the meter. A desirable apparatus may consist of a continuous reading electronic voltmeter with specified range, accuracy, and sensitivity, that is designed to operate on an input of less than 5×10^{-12} amperes when an electrode system having 1 000 megohms resistance is connected across the meter terminals, that is provided with a metal shield connected to the ground and with a satisfactory terminal to connect the shielded connection wire from the glass electrode to the meter without interference from the presence of the external electrostatic fields.

7.1.3 *Reflux Condenser and Saponification Reflux Vessel* — A suitable immersion type condenser, made to fit loosely the top of the titration beaker (*see* **7.1.1.5**) and made of chemically-resistant glass. It shall conform to

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*'Grounded' or 'Connected to the ground' means connected through a resistance of not less than 100 ohms to a standard ground potential, such as that of a water-service pipe.

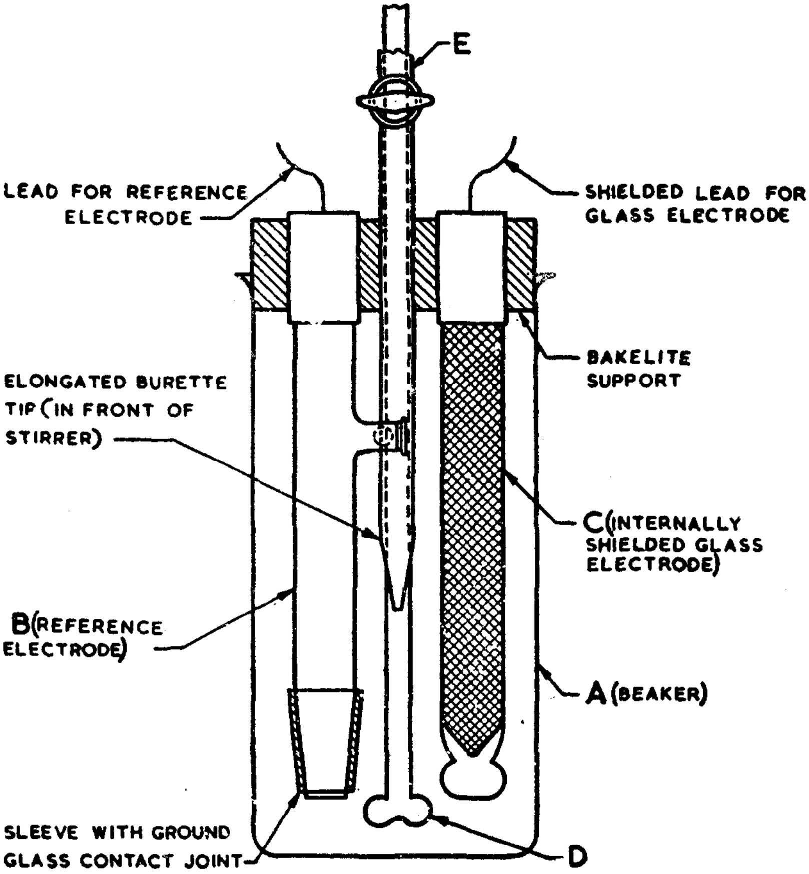
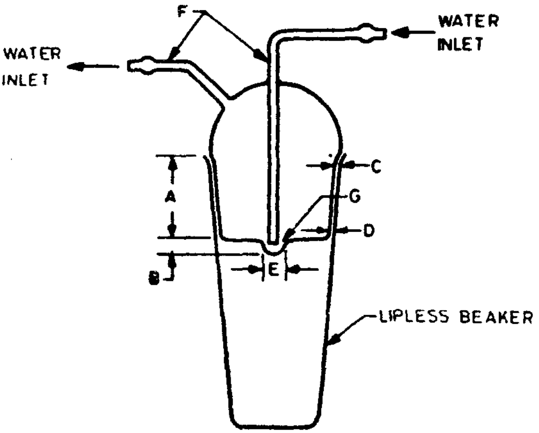

E
LEAD FOR REFERENCE ELECTRODE
SHIELDED LEAD FOR GLASS ELECTRODE
BAKELITE SUPPORT
ELONGATED BURETTE TIP (IN FRONT OF STIRRER)
C (INTERNALLY SHIELDED GLASS ELECTRODE)
B (REFERENCE ELECTRODE)
A (BEAKER)
SLEEVE WITH GROUND GLASS CONTACT JOINT
D

FIG. 2 CELL FOR POTENTIOMETRIC TITRATION

the dimensions shown in Fig. 3 except that the manner of attaching the water inlet and outlet ports may be modified as desired.

7.1.4 *Optional Saponification Reflux Vessel* — optional only for saponifications that necessitate transfer of the saponified sample to another vessel before titration A conical flask of 300-ml capacity, made of chemically resistant glass to which an adequate Allihn-type reflux condenser is attached by means of a ground-glass water-cooled joint.



A = 40 to 50 mm
B = 5 to 10 mm
C = 0·5 to 3·5 mm
D = 0·5 to 2·0 mm clearance
E = 10 to 16 mm DIA
F = 4 to 7 mm ID
G = 2 to 4 mm clearance

Fig. 3 Saponification Reflux Vessel

7.1.5 *Hot-Plate* — hot-plate, heated electrically or by steam that will maintain a mixture of 40 ml of benzene and 40 ml of *iso*propyl alcohol, contained in the saponification vessel, at active boiling temperature so that an appreciable reflux occurs.

7.2 Reagents

7.2.1 *Standard Alcoholic Potassium Hydroxide Solution* (0·1 *N*) — Add 6 g of potassium hydroxide to approximately one litre of anhydrous *iso*propyl alcohol. Boil gently for 10 minutes to effect solution. Allow the solution to stand for two days and then filter the supernatant liquid through a fine sintered glass funnel. Store the solution in a chemically-resistant glass bottle. Dispense in a manner such that the solution is protected from atmospheric carbon dioxide by means of a guard tube containing soda lime or soda asbestos (ascarite), and such that it does not come into contact with cork, rubber, or saponifiable stop-cock grease. Standardize frequently enough to detect normality changes of 0·000 5 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in carbon dioxide-free water.

7.2.2 *Standard Alcoholic Potassium Hydroxide Solution* (0·2 *N*) — Prepare, store, and standardize as directed in **7.2.1**, but use 12 to 13 g of potassium hydroxide to approximately one litre of *iso*propyl alcohol.

7.2.3 *Standard Alcoholic Hydrochloric Acid Solution* (0·1 *N*) — Mix 9 ml of hydrochloric acid (sp-gr 1·16, conforming to IS : 265-1962*) with one litre of anhydrous *iso*propyl alcohol. Standardize frequently enough to detect normality changes of 0·000 5 by potentiometric titration of approximately 8 ml (accurately measured) of the standard 0·1 N alcoholic potassium hydroxide solution diluted with 125 ml of carbon dioxide-free water.

7.2.4 *Standard Alcoholic Hydrochloric Acid Solution* (0·2 *N*) — Prepare and standardize as directed in **7.2.3**, but use 18 ml of hydrochloric acid (sp-gr 1·16, conforming to IS : 265-1962*).

7.2.5 *Titration Solvent* — Add 500 ml of benzene and 5 ml of water to 495 ml of anhydrous *iso*propyl alcohol. The titration solvent should be made up in large quantities, and its blank value determined daily by titration prior to use.

7.2.6 *Buffer Stock Solution A* — Accurately weigh 24·2 ± 0·1 g of 2-, 4-, 6-trimethyl pyridine (*Y* — collidine), and transfer to a 1-litre volumetric flask containing 100 ml of *iso*propyl alcohol. Using a 1-litre graduated cylinder, add to the flask, continuously stirring its contents, $150/N_1 \pm 5$ ml of a 0·2 N standard alcoholic hydrochloric acid solution (N_1 being the exact normality of hydrochloric acid found by standardization). Dilute to the mark with *iso*propyl alcohol, and mix thoroughly.

7.2.7 *Buffer Stock Solution B* — Accurately weigh 27·8 ± 0·1 g of *m*-nitrophenol and transfer to a 1-litre volumetric flask containing 100 ml of *iso*propyl alcohol. Using a 250-ml graduated cylinder, add to the flask while continuously stirring its contents $50/N_2 \pm 1$ ml of 0·2 N standard alcoholic potassium hydroxide solution (N_2 being the exact normality of hydrochloric acid found by standardization). Dilute to the mark with *iso*propyl alcohol, and mix thoroughly.

7.2.8 *Nonaqueous Acidic Buffer Solution* — Add 10 ml of buffer stock solution *A* to 100 ml of titration solvent. Use within one hour.

7.2.9 *Nonaqueous Basic Buffer Solution* — Add 10 ml of buffer stock solution *B* to 100 ml of titration solvent. Use within one hour.

7.2.10 *Potassium Chloride Electrolyte* — Prepare a saturated solution of potassium chloride in water.

7.2.11 *Standard Buffer Solution* — Dissolve 5·105 g of potassium acid phthalate in carbon dioxide-free water and dilute to exactly 500 ml. This solution should be prepared freshly as needed. The *pH* of this solution is taken as 4·00 at 25°C and, for the purpose of this method, is accepted as being constant at all temperatures between 15° and 35°C.

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*Specification for hydrochloric acid (*revised*)

7.3 Preparation of Electrode System

7.3.1 *Maintenance of Electrodes* — The glass electrode shall be cleaned (*see* **7.3.1.1**) at frequent intervals (not less than once every week during continual use) by immersing in cold chromic acid cleaning solution. The calomel electrode should be drained at least once every week and refilled with fresh potassium chloride electrolyte. The electrolyte level in the calomel electrode shall be kept above that of the liquid in the titration beaker at all times. When not in use, the lower halves of the electrodes shall be immersed in water and not allowed to remain immersed in titration solvent for any appreciable period of time between titrations. Although the electrodes are not extremely fragile, they should be handled carefully at all times.

7.3.1.1 Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very important in obtaining reproducible potentials, since contamination may introduce uncertain, erratic and unnoticeable liquid contact potentials. While this is of secondary importance when end points are chosen from inflection points in the titration curve, it may be quite serious when end points are chosen at arbitrarily fixed cell potentials.

7.3.2 *Preparation of Electrodes* — Before and after using, wipe the glass electrode thoroughly with a clear cloth, or a soft absorbent tissue, and rinse with water. Wipe the calomel reference electrode with a cloth or tissue, carefully remove the ground-glass sleeve, and thoroughly wipe both the ground surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joints (*see* **7.3.1.1**). Wet the ground surfaces thoroughly with electrolyte, set the sleeve firmly in place, and rinse the electrode with water. Prior to each titration, soak the prepared electrode in water for at least five minutes immediately before use, and touch the tips of the electrodes with a dry cloth or tissue to remove the excess water.

7.3.3 *Testing of Electrodes* — The meter-electrode combination shall be tested (*see* **7.3.1.1**) when first put into use, or when new electrodes are installed, and retested at intervals thereafter by dipping the electrodes into a well-stirred mixture of 100 ml of the titration solvent and 1·0 to 1·5 ml of 0·1 N standard alcoholic potassium hydroxide solution. If the meter-electrode combination is suitable for use, the potential between the electrodes will have changed by more than 0·480 V from the potential between the same electrodes when dipped in the nonaqueous acidic buffer solution.

7.4 Standardization of Apparatus — For titration of aqueous solution, as sometimes required, vary the 'asymmetry potential' adjustment until the meter registers a scale reading, in *p*H units, equal to 4·00 while the electrodes are immersed in the aqueous buffer solution at a temperature within 2 deg C of that at which the titrations are to be made.

7.4.1 To ensure comparable selection of end points when definite inflection points are not obtained in the titration curve, determine daily, for each electrode pair, the meter readings obtained with the nonaqueous acidic and basic buffer solutions (*see* Note 10). Prepare the electrode as described under **7.3**, immerse them in the nonaqueous buffer solution and stir for five minutes maintaining the temperature within 2 deg C of that at which the titrations are to be made. Read the cell voltage. The readings so obtained are taken as the end points in titration curves having no inflection points.

NOTE 10 — The response of different glass electrodes to hydrogen ion activity is not the same. Therefore, it is necessary to establish regularly for each electrode system the meter readings corresponding to the buffer solutions arbitrarily selected to represent acidic or basic end points.

7.5 Preparation of Sample of Used Oil

7.5.1 Strict observance of the sampling procedure is necessary, since the sediment itself is acidic or basic or has absorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

7.5.1.1 As used oil may change appreciably in storage, samples should be tested as soon as possible after removal from the lubricating system; and the dates of sampling and testing should be noted.

7.5.2 Heat the sample (*see* **7.5.2.1**) of used oil to 60° ± 5°C in the original container until all of the sediment is homogeneously suspended in the oil. If the original container is a can, or if it is glass and more than three-fourths full, transfer the entire sample to a clear-glass bottle having a capacity at least one third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container.

7.5.2.1 When samples are visibly free from sediment, the heating procedure described in **7.5.2** may be omitted.

7.5.3 After complete suspension of all sediment, strain the sample or a convenient aliquot, through 150-micron IS sieve for the removal of large contaminating particles.

7.6 Procedure — Two procedures, namely, general procedure and direct titration procedure, have been prescribed. The 'general procedure' is intended for samples of unknown saponification characteristics or of samples that, upon saponification, produce a precipitate that clings to the surface of the reflux vessel. The direct titration procedure may be used for samples of known saponification characteristics and for samples that do not produce upon saponification, a precipitate that clings to the surface of the reflux vessel.

7.6.1 *General Procedure* — Introduce into a 300-ml titration beaker, a weighed quantity of sample as given in Table 1 and add 40 to 45 ml of benzene. From a 50-ml burette, add 40·00 ± 0·05 ml of standard alcoholi potassium hydroxide solution (0·2 N) allowing 60 to 80 seconds to elaps between adding the first 39·5 ml and the final 0·5 ml. Place the reflux condenser in the beaker, cool the condenser by passing tap water through it at a temperature less than 35°C and heat on a hot-plate at refluxing temperature for 110 to 120 minutes after refluxing begins.

NOTE 11 — If the optional saponification vessel is used, do not use grease on the ground-glass joints, but moisten it with *iso*propyl alcohol to prevent 'freezing' of the joint.

7.6.1.1 Disconnect the condenser and wash the exposed condenser and beaker surfaces with 10 to 20 ml of titration solvent.

7.6.1.2 While the contents of the saponification beaker are still hot, quickly transfer the liquid phase by decantation to a second 250-ml titration beaker, rinsing the saponification beaker and insoluble residue with three 5-ml portions of titration solvent, add the rinsings to the second beaker, cover with a watch-glass and cool the beaker and contents to room temperature. Add 100 ml of carbon dioxide-free water to the original saponification beaker without delay after separation, and heat just to boiling. Cover the beaker with a watch-glass and cool to room temperature. Titrate the solutions as directed in **7.6.1.3** to **7.6.1.7** within 2 hours after the end of the saponification period.

TABLE 1 SIZE OF SAMPLE

(*Clause* 7.6.1)

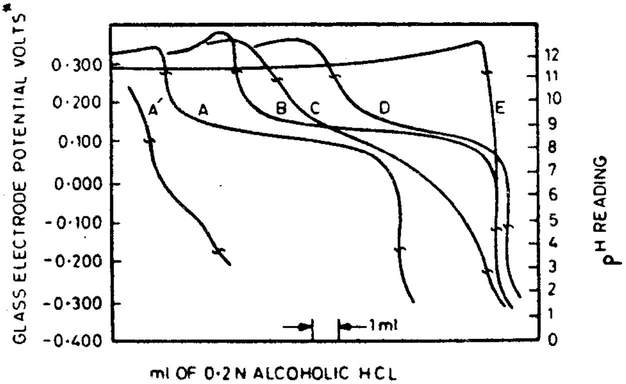
SAPONIFICATION NUMBER (1)	SIZE OF SAMPLE (2)	SENSITIVITY OF WEIGHING (3)
	g	g
Up to 5·0	20·0 ± 2·0	0·05
Above 5·0 to 30·0	5·0 ± 0·5	0·02
,, 30·0 ,, 80·0	2·0 ± 0·2	0·01
,, 80·0 ,, 200	0·8 ± 0·1	0·005
,, 200	0·50 ± 0·05	0·002

If the appropriate sample size is too large to form a homogeneous solution a smaller size sample may be taken. It shall be recognized, however, that the precision and accuracy may suffer accordingly.

7.6.1.3 Prepare the electrodes as described under **7.3.** Place the beaker containing the nonaqueous test solution on the titration stand and adjust its position so that the electrodes are about half immersed. Start the stirrer, and stir throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution.

7.6.1.4 Fill the 50-ml burette with standard alcoholic hydrochloric acid solution (0·2 N) and place the burette in position in the titration assembly, taking care that the tip is immersed about 25 mm in the liquid in the beaker. Record the initial burette and meter readings. Add standard alcoholic hydrochloric acid cautiously but rapidly as long as the meter reading remains constant or changes only slightly. Stop the addition of standard alcoholic hydrochloric acid momentarily after every 1 or 2 ml, to allow the potential to become constant.

7.6.1.5 Upon approaching the first inflection (*see* Fig. 4) gradually decrease the size of the increments of standard alcoholic hydrochloric acid and start recording burette and corresponding meter readings (*see* Note 12). Add suitable small portions of alcoholic hydrochloric acid, waiting after each addition for a constant meter reading to be established (*see* Note 13). In any regions where 0·1 ml of standard alcoholic hydrochloric acid (0·2 N) produces a total change of more than 0·030 V (corresponding to 0·5 *p*H unit) in the meter reading, add 0·1-ml portions. In the intermediate regions (plateaus) where 0·1 ml changes the meter reading less than 0·030 V, add larger portions sufficient to produce a total potential change approximately equal to, but not greater than 0·030 V; however, do not add



A = Blown rapeseed oil, solvent curve
A′ = Blown rapeseed oil, water curve
B = Castor oil, direct titration curve
C = Black oxidized motor oil, direct titration curve
D = Material exhibiting base saponification number
E = Blank, direct titration curve

*On some meters the voltage sign is reversed.

FIG. 4 ILLUSTRATIVE TITRATION CURVES

less than 0·1 ml or more than 0·5-ml portions of standard alcoholic hydrochloric acid solution.

NOTE 12 — In titrating the benzene *iso*propyl alcohol solution the inflection in the titration curve is generally imminent when the potential ceases to increase steadily for each portion of acid added and shows a small sudden increase, or develops a tendency to waver. This point is the characteristic 'peak' in the titration curve immediately before the first inflection (*see* Fig. 4, Curve E). A further warning of the impending inflection is the tendency for the potential to decrease somewhat upon the addition of a small portion of acid and then to return to the previous reading.

NOTE 13 — Consider the cell potential constant when it changes less than 0·005 V (corresponding to 0·1 *p*H scale unit) per minute. This may require approximately 1 to 2 minutes per 0·1-V change in potential (corresponding to 1·7 *p*H scale units) when adding 0·01-ml increments.

7.6.1.6 Continue the titration in the above manner until the meter reading changes less than 0·005 V (corresponding to 0·1 *p*H unit) per 0·1 ml of titrant and the meter reading indicates that the solution is more acidic than the nonaqueous acidic buffer. Remove the titrated solution, rinse the electrodes with *iso*propyl alcohol, and immerse them in water.

7.6.1.7 Titrate the water solution preferably using the *p*H scale of the meter (*see* Note 14). Add 0·1-ml portions of the hydrochloric acid solution for the first three increments and then, if necessary, add larger portions sufficient to produce a total meter reading change approximately equal to, but not greater than 0·5 *p*H unit; however, do not add less than 0·1-ml portions of the hydrochloric acid solution. Titrate in this manner until the meter reading change is less thon 0·1 *p*H unit and is at a scale reading of 3·5 *p*H units or lower. Remove the titrated solution and immerse the electrodes in water.

NOTE 14 — If the water solution has little or no colour, the titration of this solution may be carried out colorimetrically using phenolphthalein and methyl orange indicators to indicate end points at *p*H of 8·2 and 5·0, respectively. Titrate to the phenolphthalein end point before adding methyl orange.

7.6.1.8 *Blank determinations* — Simultaneously with each set of sample determinations, make duplicate blank determinations, following exactly the procedure used for the sample determinations (except for omission of the sample). Always use identical reagents for the blank determination and for the sample determination.

7.6.2 *Direct Titration Procedure* — For samples of known saponification characteristics and for samples that do not produce, upon saponification, a precipitate that clings to the surface of the reflux vessel, saponify the sample and rinse the condenser as in **7.6.1** and **7.6.1.1**. Without transfer of the saponification solution, cover the beaker with a watch-glass, cool to room temperature, and titrate with alcoholic hydrochloric acid solution (0·2 N) directly in the saponification beaker within 2 hours after the end of the saponification period. In all other respects, conduct the determination as specified in **7.6.1**, except to omit the preparation and titration of the water solution.

7.7 Calculation and Reporting

7.7.1 Plot the volumes of standard alcoholic hydrochloric acid solution (0·2 N) against the corresponding meter readings (*see* Fig. 4) for each titration and for the blank (*see* Note 15).

NOTE 15 — When the solvents used are pure, the blank nonaqueous or aqueous titration curves may exhibit a single straight line break and may not show two inflection points. When this condition is approached, end points may be marked at the values corresponding to readings obtained using the two nonaqueous buffers.

7.7.2 On the curves for the sample titrated in benzene-*iso*propyl alcohol solution, mark as an end point any inflection point (*see* Note 12) that occurs near the cell voltages representing the nonaqueous acidic and basic buffers. If no inflection point appears (*see* Note 16), mark the end points at those meter readings corresponding to the two nonaqueous buffers.

NOTE 16 — An inflection point is generally recognizable by inspection whenever several successive 0·10-ml increments each produce a cell potential change greater than 0·015 V or 0·25 *p*H scale units and at least 30 percent greater than those produced by previous and subsequent increments of the same size. Generally, definite inflection points may be discerned only in regions where increments of the same size are used.

7.7.3 On the curves for the titration in aqueous medium, mark the inflection point, or if there is none, the end point, that occurs near or at a *p*H scale reading of 8·2 and 5·0 respectively. On the curve for titration of the blank, mark or select as the end point the volume of titrant at the same voltage or meter reading as that selected for the sample titration.

7.7.4 Calculate the saponification value as follows:

$$S = \frac{56 \cdot 1\ (B + D - A - C)\ N}{W}$$

where

S = the saponification value of the sample,

B = value corresponding to A but for the blank titration,

D = value corresponding to C but for the blank titration,

A = volume in ml of standard alcoholic hydrochloric acid solution required to neutralize the basic material in the titration of the nonaqueous saponified solution of the sample to the end point that occurs at a meter reading corresponding to that of the alkaline nonaqueous buffer,

C = volume in ml of standard alcoholic hydrochloric acid solution required to neutralize the basic material in the titration of the water solution to the end point at which the *p*H scale reading is approximately equal to 8·2,

N = normality of standard alcoholic hydrochloric acid solution, and

W = weight in g of the sample used.

7.7.5 *Reporting* — Report the calculated figure as the saponification value (**P : 55**) Method C.

7.8 Precision

7.8.1 *Good Inflection in Titration Curve* — When good inflections are obtained in the titration curves, result shall not differ from the mean by more than the following amounts:

Saponification Value	*Repeatability*	*Reproducibility*
Up to 5·0	0·1	0·4
Above 5·0	2 percent of mean	8 percent of mean

7.8.2 *Poor Inflection in Titration Curve* — When poor inflections are obtained in the titration curves, the values for repeatability and reproducibility will be larger than those given in **7.8.1**.

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